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(54) HIGH POLYMER ELECTROLYTE MEMBRANE REINFORCED SUBSTRATE AND HIGH POLYMER ELECTROLYTE MEMBRANE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high polymer electrolyte membrane reinforced substrate for solid high polymer type fuel cell improved oxidation resistance, acid resistance, and hydrolysis resistance, and to provide a high polymer electrolyte membrane, provided with proton conductivity, strength and heat resistance, using the base material.

SOLUTION: This high polymer electrolyte membrane reinforced substrate consists of a porous sheet made of aramid resin, and the porous sheet is coated with fluororesin. As the porous sheet, nonwoven fabric of aramid resin is highly suited to use for this purpose.

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CLAIMS

[Claim(s)]

[Claim 1] It is the polyelectrolyte film reinforcement base material which consists of a porous sheet which consists of an aramid resin, and is characterized by coating this porous sheet with the fluororesin.

[Claim 2] The polyelectrolyte film reinforcement base material according to claim 1 characterized by a porous sheet being a nonwoven fabric.

[Claim 3] The polyelectrolyte film reinforcement base material according to claim 1 or 2 to which a polytetrafluoroethylene (PTFE) comes out and the principal component of a fluororesin is characterized by a certain thing.

[Claim 4] The polyelectrolyte film reinforcement base material according to claim 2 or 3 coated with the front face of the fiber which constitutes a nonwoven

fabric by the fluororesin.

[Claim 5] The manufacturing method of the polyelectrolyte film reinforcing materials characterized by for the porous sheet which consists of an aramid resin infiltrating the water dispersion of a fluororesin, and subsequently heat-treating.

[Claim 6] The manufacturing method of the polyelectrolyte film reinforcement base material according to claim 5 characterized by heat treatment temperature being 380 degrees C or less beyond the melting point of this fluororesin.

[Claim 7] The manufacturing method of the polyelectrolyte film reinforcement base material according to claim 6 characterized by the fluororesin solid-content concentration of the water dispersion of this fluororesin being 10 - 50 % of the weight.

[Claim 8] It is the proton conductivity polyelectrolyte film which consisted of a porous sheet which consists of an aramid resin, and was reinforced with the polyelectrolyte film reinforcement base material characterized by coating this porous sheet with the fluororesin.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the polyelectrolyte film

reinforcement base material excellent in mechanical strength and thermal resistance, and the proton conductivity polyelectrolyte film reinforced by that cause, in more detail, this invention consists of a porous sheet of an aramid resin, and relates to the proton conductivity polyelectrolyte film reinforced with the polyelectrolyte film reinforcement base material which raised oxidation resistance, acid resistance, and adding-water-proof resolvability, its manufacturing method, and this reinforcement base material.

[0002]

[Description of the Prior Art] An aramid fiber is excellent in thermal resistance or intensity, and is used for the use for which those properties are needed. However, the present condition is fully being able to finishing harnessing with the feature which a use's is limited since [, such as oxidation resistance, acid resistance, and adding-water-proof resolvability,] it is inferior chemical-resistant, and aramid fibers', such as thermal resistance's and intensity's, have.

[0003] In recent years, a fuel cell attracts attention as a clean and efficient power supply from an environmental problem, and development of a solid-state macromolecule type fuel cell (PEFC) is actively performed from a viewpoint of a low-temperature operation or a miniaturization. The polyelectrolyte film

which PEFC uses is "Nafion" (Nafion, registered trademark of Du Pont.). the following -- the same . Although the perfluoro sulfonic-acid film represented is used, thin film-ization is demanded from viewpoints, such as reduction of a membrane resistance, film moisture maintenance management nature, and low-cost-izing. It is the mechanical strength-problem of a perfluoro sulfonic-acid film, and film reinforcement technology becomes important . for thin-film-izing. The technology of making it composite-ize with a tetrafluoroethylene extension porous membrane as film reinforcement technology is indicated by JP,8-162132,A. However, since the surface tension of a tetrafluoroethylene extension porous membrane was small, it it is not only expensive as a base material, but had the problem that sinking [of a dope] in was difficult, from the wettability problem of a dope at the time of electrolyte dope sinking in.

[0004] The demand to the oxidation resistance from a viewpoint of endurance is strong to the polyelectrolyte film reinforcement base material for PEFC, and the present condition is that only the fluorine system resin represented by the tetrafluoroethylene is used.

[0005] On the other hand, there is technology coated with a fluororesin as technology which raises the chemical resistance of an aramid fiber. For

example, make a non-subtlety particle adhere, the mixture of the water dispersion of a polytetrafluoroethylene particle and fluorination urethane is made to adhere after heat treatment, and there is rope-like matter (JP,3-249276,A) heat-treated at the method (JP,8-299719,A) of heat-treating and **60 degrees C of melting points of a fluororesin.

[0006]

[Problem(s) to be Solved by the Invention] It is in the purpose of this invention offering the aramid porosity sheet with which oxidation resistance, acid resistance, and adding-water-proof resolvability have been improved, and offering the polyelectrolyte film for PEFC which has proton conductivity, intensity, and thermal resistance by using this as a polyelectrolyte film reinforcement base material for PEFC.

[0007]

[Means for Solving the Problem] The nonwoven fabric of excelling the fluorine system resin system in intensity which consists of the viewpoint of thin-film-izing of the polyelectrolyte film for PEFC to an aramid fiber is advantageous as a reinforcement base material. Moreover, it is advantageous also in cost. However, oxidation resistance, acid resistance, and adding-water-proof resolvability pose a problem.

[0008] As a result of inquiring

wholeheartedly in view of such the present condition, the porous sheet which consists of an aramid resin excellent in oxidation resistance, acid resistance, and adding-water-proof resolvability is developed, and it came to complete this invention by using this as a polyelectrolyte film reinforcement base material for PEFC.

[0009] That is, this invention consists of a porous sheet which consists of an aramid resin, and this porous sheet is a polyelectrolyte film reinforcement base material characterized by being coated with the fluororesin.

[0010] Oxidation resistance, acid resistance, and adding-water-proof resolvability improve on the porous sheet which consists of an aramid resin by giving fluororesin coating, and this invention uses this for it as a polyelectrolyte film reinforcement base material in order to solve the above-mentioned technical problem.

[0011]

[Embodiments of the Invention] Hereafter, the polyelectrolyte film reinforcement base material and polyelectrolyte film of this invention are explained in detail. The polyelectrolyte film reinforcement base material of this invention is characterized by being the porous sheet which consists of an aramid resin coated with the fluororesin.

[0012] Although there are some which consist of a meta-mold aramid resin and

a Para type aramid resin in the aramid resin which forms the porous sheet used for the polyelectrolyte film reinforcement base material of this invention, it can use for this invention also with both. Moreover, it does not matter even if it is the copolymer or blend object with which a principal component consists of an aramid resin.

[0013] paper with the permeability of the structure which has the shape of a three-dimensions mesh which the configuration of the porous sheet which consists of an aramid resin turns into from an aramid fiber in this invention, such as a nonwoven fabric and textiles, and the synthetic pulp which is an aramid polymer distribute -- the configuration of the film which much pores which consist of a sheet [like] or an aramid resin opened is desirable The nonwoven fabric of 5 - 40 g/m² is suitably used for a superintendent officer from a viewpoint of the proton conductivity of the electrolyte film reinforced by the ease of carrying out and this reinforcement base material of electrolyte film production which were especially reinforced by these reinforcement base materials, such as the ease of carrying out of coating, the impregnating ability of a polyelectrolyte dope, and the amount of sinking in. Intensity as a reinforcement base material cannot fully be maintained as a superintendent officer is less than two 5 g/m. Moreover, if a superintendent

officer is larger than 40 g/m², thickness will become thick and the voidage of a nonwoven fabric will also fall. For this reason, a membrane resistance becomes large and causes the fall of the conductivity of a polyelectrolyte film.

[0014] The fluororesin which makes a polytetrafluoroethylene (PTFE) and this a principal component as a fluororesin which coats the porous sheet which consists of an aramid resin is used suitably. As a fluororesin which makes PTFE a principal component (50% of the weight or more of the whole preferably 80 % of the weight or more), although tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) and tetrafluoroethylene-hexafluoropropylene copolymer (FEP) ** is used suitably, for example, it is not limited to this.

[0015] It is observable whether the porous sheet which consists of an aramid resin is coated with the fluororesin with an optical microscope and an electron microscope. Moreover, it can check also by the general surface analysis method of the Raman spectrometry. The amount of coating of a fluororesin can be estimated by measuring the weight before and behind coating.

[0016] As for the polyelectrolyte film reinforcement base material of this invention, it is desirable that average thickness is [air permeability] two or less cc-in [10sec(s)/100 cc-in] air permeability in 80 micrometers or less. If

thickness exceeds 80 micrometers, although intensity goes up, since the thickness of the polyelectrolyte film reinforced by the polyelectrolyte film reinforcement base material of this invention becomes thick, it increases [because the degree of swelling to the water of an electrolyte film falls / a membrane resistance] and is not desirable. Air permeability shows the value measured with Gurley method (time taken for 100 cc air to penetrate 1 inch of area of 2 by the pressure of 2.3cmHg(s)). If this value is larger than 10sec(s) / 100 cc-in², while composite-ization of the polyelectrolyte by the coating method becomes difficult, it will become difficult from a polymer solution to also fully raise proton conductivity.

[0017] The water dispersion of a fluororesin is infiltrated into the porous sheet which consists of a ** aramid resin although especially a limit does not have the manufacturing method of the polyelectrolyte film reinforcement base material of this invention, and it heat-treats, and the water dispersion of a fluororesin is infiltrated into the method and ** aramid fiber which coat this porous sheet with a fluororesin, it heat-treats, this fiber front face is coated with a fluororesin, and the method of a nonwoven fabric etc. carrying out a porous sheet using the obtained fiber, and making this this reinforcement base

material is mentioned. Here, the simplicity of manufacture etc. to the former is desirable. Hereafter, this method is explained.

[0018] The water dispersion of a fluororesin is infiltrated into the porous sheet which consists of this aramid resin, and it heat-treats, and as a method of coating this porous sheet with a fluororesin, a fluorine system resin water dispersion is infiltrated into an aramid nonwoven fabric, and an excessive fluororesin water dispersion is removed by drawing through with a roller, for example. After air-drying this, it heat-treats below 380 degrees C beyond the melting point of a fluororesin. Since a thermal contraction starts at the time of heat treatment, fixing with metal mold etc. is desirable. It is more desirable to carry out in the environment where the oxygen under nitrogen-gas-atmosphere mind etc. does not exist, although heat treatment may be performed in air. When oxygen exists, during heat treatment, the porous sheet which consists of an aramid resin may oxidize, and discoloration and the fall of physical properties may be caused. After [heat treatment] water cooling is carried out, and it cools rapidly. The polyelectrolyte film reinforcement base material in this invention is producible by air-drying this.

[0019] 10 - 50 % of the weight is suitable for the fluororesin solid-content concentration of this fluororesin water

dispersion used for coating. The front face of the resin (fiber which constitutes it in the case of a nonwoven fabric) which constitutes the porous sheet with which fluororesin solid-content concentration becomes being less than 10 % of the weight from an aramid resin cannot be enough worn by the fluororesin, and oxidation resistance is not fully improved. Moreover, it becomes [if fluororesin solid-content concentration is larger than 50 % of the weight, will close the hole of the porous sheet with which a fluororesin consists of an aramid resin, and / a proton conductivity polyelectrolyte and composite-ization] difficult and is not desirable. Moreover, even if it can carry out [****]-izing, a membrane resistance increases and an electrical property is not desirable.

[0020] Although it heat-treats after infiltrating a fluororesin water dispersion into the porous sheet which consists of an aramid resin, it is desirable to perform heat treatment below 380 degrees C beyond the melting point of a fluororesin. It is difficult for a fluororesin not to dissolve that it is under the melting point of a fluororesin, but to fully wear the front face of a porous sheet by the fluororesin. Here, the front face of the hole inside a sheet, and in the case of a nonwoven fabric, with the front face of a porous sheet, the front face of each fiber is included in addition to both the front faces of a porous sheet. Moreover, if it

heat-treats at temperature higher than 380 degrees C, the pyrolysis of the porous sheet applied during heat treatment will start, and the fall of physical properties will be caused. Heat treatment time has 3 - 10 desirable minutes. There is not sufficient time to coat a front face with the fluororesin which adhered that it was less than 3 minutes to the resin front face fusing and flowing. Moreover, if longer than 10 minutes, degradation of this porous sheet will start with heat treatment, and a problem will arise in respect of physical properties.

[0021] Thus, the obtained porous sheet is substantially covered by the fluororesin by the grade by which oxidation resistance is fully improved, and, as for air permeability, what is two or less 10sec(s)/100 cc-in is desirable from a viewpoint of an electrical property.

[0022] The proton conductivity polyelectrolyte film reinforced by this polyelectrolyte film reinforcement base material is described.

[0023] This proton conductivity polyelectrolyte film is complex with which it comes to put the above-mentioned poly membrane reinforcement base material and proton conductivity polymer together, and the point of having the dynamic thermal resistance of 300 degrees C or more is the feature. Dynamic heat-resistant temperature can be measured by mechanical thermal property analysis

(TMA). Here, the temperature up of the temperature was carried out to this proton conductivity polyelectrolyte film (the thickness of about 45mm, width of face of 5mm, the shape of a strip of paper with a length of 25mm) the speed for 10-degree-C/by the 1g load, and temperature to which a film fractures or a film is extended 10% was made into dynamic heat-resistant temperature. It becomes impossible for this temperature to guarantee the safety of the cell at the time of less than 300 degrees C covering the expenses of the temperature inside a cell rapidly by the anomalous reaction etc., and it is not desirable.

[0024] This proton conductivity polyelectrolyte film can infiltrate proton conductivity polymer for example, into the above-mentioned polyelectrolyte film reinforcement base material, and can be manufactured by drying. Although the polysulfone into which the perfluoro sulfonic acid type resin represented by "Nafion" as proton conductivity polymer, polystyrene sulfonate, and the sulfonic group were introduced, polyether sulphone, a polysulfone, etc. are mentioned, it is not limited to these.

[0025]

[Example] Hereafter, although the content of this invention is explained in detail using an example, this invention is not limited to these examples.

The oxidation-resistant appraisal method in a <oxidation-resistant model

evaluation> example is described. However, oxidation-resistant evaluation is not limited to this. Although this invention has coated the aramid nonwoven fabric with the fluororesin for improvement in oxidation resistance, oxidation-resistant evaluation of a nonwoven fabric is "Proceedings of the Symposium - Electrode Materials and Process for Energy Conversion and Storage", Vol.77(6), p.314 (1977), and The Electrochemical Society was made reference. A nonwoven fabric is immersed into the so-called Fenton reagent which mixed a 20 ppm iron sulfate (II) and (FeSO₄) with 30% of the weight of hydrogen peroxide solution, and it heat-treats at 68 degrees C. Thus, aging of the **** maximum stress of the processed nonwoven fabric can estimate the oxidation resistance of a nonwoven fabric. **** maximum stress pulls and is the maximum stress in an examination. The value (percentage shows) which broke the **** maximum stress of the nonwoven fabric after 24-hour heat treatment by **** maximum stress of an unsettled nonwoven fabric was made into the **** maximum-stress maintenance factor, and this was made into the oxidation-resistant index.

[0026] The average thickness which consists of a [example 1] meta-mold aramid fiber (tradename : Conex, Teijin, Ltd. make) produced the nonwoven fabric of 20 g/m² by 40 micrometers, the

superintendent officer produced by the dry type milling-paper method, the polytetrafluoroethylene (PTFE, 327 degrees C of melting points) water dispersion (Daikin Industries make) whose solid-content concentration is 30% was infiltrated into this, and it was made air-dry [draw through and] with a roller. This nonwoven fabric was fixed to metal mold, heat treatment was performed for 10 minutes at 340 degrees C, and the polyelectrolyte film reinforcement base material was produced. The average thickness of this polyelectrolyte film reinforcement base material was 50 micrometers, and air permeability was 0.1sec(s) / 100 cc-in². Evaluation oxidation-resistant by method which was described about this nonwoven fabric in the top was performed. The **** maximum-stress maintenance factor was 84.6%. A result is shown in drawing 1.

[0027] The average thickness which consists of a [example 2] meta-mold aramid fiber (tradename : Conex, Teijin, Ltd. make) produced the nonwoven fabric of 20 g/m² by 40 micrometers, the superintendent officer produced by the dry type milling-paper method, the tetrafluoroethylene-hexafluoropropylene copolymer (FEP, 270 degrees C of melting points) water dispersion (Daikin Industries make) whose solid-content concentration is 30% was infiltrated into this, and it was made air-dry [draw through and] with a roller. This

nonwoven fabric was fixed to metal mold, heat treatment was performed for 10 minutes at 300 degrees C, and the polyelectrolyte film reinforcement base material was produced. The average thickness of this polyelectrolyte film reinforcement base material was 50 micrometers. Air permeability is 0.1sec(s) / 100 cc-in². Evaluation oxidation-resistant by method which was described about this nonwoven fabric in the top was performed. The **** maximum-stress maintenance factor was 81.3%. A result is shown in drawing 1.

[0028] The average thickness which consists of a [example 1 of comparison] meta-mold aramid fiber (tradename : Conex, Teijin, Ltd. make) produced the nonwoven fabric of 20 g/m² by 40 micrometers, the superintendent officer produced by the dry type milling-paper method, and evaluation oxidation-resistant by method which was described in the top was performed. 0.04sec(s) / 100 cc-in², and the **** maximum-stress maintenance factor of the air permeability of this nonwoven fabric were 27.3%. A result is shown in drawing 1. As for the aramid nonwoven fabric which coated the fluororesin which is the polyelectrolyte film reinforcement base material of this invention, compared with an aramid nonwoven fabric, oxidation resistance has been clearly improved from examples 1 and 2 and the example 1 of comparison.

[0029] It produced in the [example 3] example 1, the polyelectrolyte film reinforcement base material was placed on the polyethylene-terephthalate film, and the cast of the Nafion solution (Aldrich) of 10wt(s).% was carried out by the doctor knife of 200-micrometer path clearance from on the. Subsequently, the proton conductivity polyelectrolyte film reinforced with this reinforcement base material was produced by air-drying this. The dynamic heat-resistant temperature of this proton conductivity polyelectrolyte film was 400 degrees C or more. As a result of performing evaluation oxidation-resistant by method which was described about this proton conductivity electrolyte film in the top, the **** maximum-stress maintenance factor was 82.1%.

[0030] It produced in the [example 4] example 2, the polyelectrolyte film reinforcement base material was placed on the polyethylene-terephthalate film, and the cast of the Nafion solution (Aldrich) of 10wt(s).% was carried out by the doctor knife of 200-micrometer path clearance from on the. The proton conductivity polyelectrolyte film reinforced with this reinforcement base material according to it being air-dry was produced. The dynamic heat-resistant temperature of this proton conductivity polyelectrolyte film was 400 degrees C or more. As a result of performing evaluation oxidation-resistant by method

which was described about this proton conductivity electrolyte film in the top, the **** maximum-stress maintenance factor was 79.4%. Maintaining oxidation resistance also with the proton conductivity electrolyte film equivalent to the polyelectrolyte film reinforcement base material of this invention which made the polyelectrolyte film reinforcement base material of this invention composite-ize with perfluoro sulfonic acid type resin from examples 3 and 4 was shown. And compared with an aramid nonwoven fabric, as for the aramid nonwoven fabric which coated the fluororesin, acid resistance and adding-water-proof resolvability have also been improved.

[0031] This was pierced and used for the diameter of 30mm using the electrode made from U.S. E-TEKINC which made the platinum of 0.38 mg/cm² support as a [example 5] gas diffusion electrode. After being immersed for 2 hours into the ion exchange water which boiled the polyelectrolyte film obtained in the example 3 and making this film into a water state, water with a superfluous front face was wiped off, and it put by these two gas diffusion electrodes, and pressurized for 3 minutes by 9.8MPa(s) (100 kgf/cm²) at 100 degrees C, and the electrode zygote was obtained. About the obtained electrode zygote, humidification hydrogen and oxygen were supplied and fuel cell output characteristics were

evaluated under 80-degree-C heating. Although ten single cells were produced, defects, such as a short circuit and a gas leak, do not have one, and the performance of 0.65V was obtained by 0.7 A/cm².

[0032]

[Effect of the Invention] As explained in full detail above, the oxidation resistance of the porous sheet which consists of an aramid resin by coating with a fluororesin according to this invention, acid resistance, and adding-water-proof resolvability were raised, and it became possible to use especially the porous sheet which consists of an aramid resin as a suitable polyelectrolyte film reinforcement base material for solid-state macromolecule type fuel cells.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 shows aging of the **** maximum stress in oxidation-resistant evaluation of the nonwoven fabric of examples 1 and 2 and the examples 1 and 2 of comparison.

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(54)【発明の名称】 高分子電解質膜補強基材及び高分子電解質膜

(57)【要約】

【課題】 耐酸化性、耐酸性、耐加水分解性の改善された固体高分子型燃料電池用の高分子電解質膜補強基材、及びこれを用いたプロトン伝導性、強度、耐熱性を兼ね備えた高分子電解質膜を提供することにある。

【解決手段】 アラミド樹脂からなる多孔性シートからなり、該多孔性シートはフッ素樹脂でコーティングされていることを特徴とする高分子電解質膜補強基材であり、多孔性シートとしてアラミド樹脂の不織布を用いることが好適である。

【特許請求の範囲】

【請求項 1】 アラミド樹脂からなる多孔性シートからなり、該多孔性シートはフッ素樹脂でコーティングされていることを特徴とする高分子電解質膜補強基材。

【請求項 2】 多孔性シートが不織布であることを特徴とする請求項 1 記載の高分子電解質膜補強基材。

【請求項 3】 フッ素樹脂の主成分がポリテトラフルオロエチレン (PTFE) がであることを特徴とする請求項 1 または 2 記載の高分子電解質膜補強基材。

【請求項 4】 不織布を構成する繊維の表面がフッ素樹脂でコーティングされている請求項 2 または 3 記載の高分子電解質膜補強基材。

【請求項 5】 アラミド樹脂からなる多孔性シートにフッ素樹脂の水分散液を含浸させ、ついで熱処理することを特徴とする高分子電解質膜補強材の製造法。

【請求項 6】 熱処理温度が該フッ素樹脂の融点以上 380℃以下であることを特徴とする請求項 5 記載の高分子電解質膜補強基材の製造法。

【請求項 7】 該フッ素樹脂の水分散液のフッ素樹脂固形分濃度が 10～50 重量%であることを特徴とする請求項 6 記載の高分子電解質膜補強基材の製造法。

【請求項 8】 アラミド樹脂からなる多孔性シートからなり、該多孔性シートはフッ素樹脂でコーティングされていることを特徴とする高分子電解質膜補強基材で補強されたプロトン伝導性高分子電解質膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は機械強度と耐熱性に優れた高分子電解質膜補強基材及びそれにより補強されたプロトン伝導性高分子電解質膜に関するもので、さらに詳しくは、アラミド樹脂の多孔性シートからなり、耐酸化性、耐酸性、耐加水分解性を向上させた高分子電解質膜補強基材、その製造法及び該補強基材で補強されたプロトン伝導性高分子電解質膜に関するものである。

【0002】

【従来の技術】 アラミド繊維は耐熱性や強度に優れ、これらの性質が必要とされる用途に用いられる。しかし耐酸化性、耐酸性及び耐加水分解性といった耐薬品性に劣ることから用途が限定され、耐熱性や強度といったアラミド繊維のもつ特徴と十分に活かされていないのが現状である。

【0003】 近年、環境問題からクリーンで高効率な電源として燃料電池が注目され、低温作動や小型化の観点から固体高分子型燃料電池 (PEFC) の開発が活発におこなわれている。PEFC の用いる高分子電解質膜は「ナフィオン」(Nafion、デュボン社の登録商標。以下同様。) に代表されるパーフルオロスルホン酸膜が用いられているが、膜抵抗の低減、膜水分保持管理性、低コスト化等の観点から薄膜化が要求されている。パーフルオロスルホン酸膜の機械強度的な問題であり、

薄膜化のためには膜補強技術が重要となってくる。特開平 8-162132 号公報には、膜補強技術としてテトラフルオロエチレン延伸多孔膜と複合化させるという技術が記載されている。しかし、テトラフルオロエチレン延伸多孔膜は支持体として高価だけでなく、その表面張力が小さいために、電解質ドープ含浸のときドープの濡れ性の問題からドープの含浸が難しいという問題を有していた。

【0004】 PEFC 用高分子電解質膜補強基材には耐久性といった観点から耐酸化性に対する要求は強く、テトラフルオロエチレンに代表されるフッ素系樹脂しか用いられていないのが現状である。

【0005】 他方、アラミド繊維の耐薬品性を向上させる技術としてフッ素樹脂でコーティングする技術がある。例えば、無機微粒子を付着させ、熱処理後、ポリテトラフルオロエチレン微粒子の水分散液とフッ素化ウレタンとの混合物を付着させ、熱処理する方法 (特開平 8-299719 号公報)、フッ素樹脂の融点 ±60℃ で熱処理したロープ状物質 (特開平 3-249276 号公報) がある。

【0006】

【発明が解決しようとする課題】 本発明の目的は耐酸化性、耐酸性、耐加水分解性の改善されたアラミド多孔性シートを提供し、これを PEFC 用高分子電解質膜補強基材として用いることでプロトン伝導性、強度、耐熱性を兼ね備えた PEFC 用高分子電解質膜を提供することにある。

【0007】

【課題を解決するための手段】 PEFC 用高分子電解質膜の薄膜化の観点から、アラミド繊維からなる不織布は強度的にフッ素系樹脂系より優れていることは補強基材として有利である。また、コスト的にも有利である。しかし、耐酸化性、耐酸性、耐加水分解性が問題となる。

【0008】 このような現状を鑑み鋭意検討した結果、耐酸化性、耐酸性、耐加水分解性に優れたアラミド樹脂からなる多孔性シートを開発し、これを PEFC 用高分子電解質膜補強基材として利用することで、本発明を完成するに至った。

【0009】 すなわち本発明は、アラミド樹脂からなる多孔性シートからなり、該多孔性シートはフッ素樹脂でコーティングされていることを特徴とする高分子電解質膜補強基材である。

【0010】 本発明は、上記の課題を解決するためアラミド樹脂からなる多孔性シートにフッ素樹脂コーティングを施すことで耐酸化性、耐酸性、耐加水分解性の改善し、これを高分子電解質膜補強基材として用いる。

【0011】

【発明の実施の形態】 以下、本発明の高分子電解質膜補強基材及び高分子電解質膜について詳細に説明する。本発明の高分子電解質膜補強基材はフッ素樹脂でコーティ

ングされたアラミド樹脂からなる多孔性シートであることを特徴とする。

【0012】本発明の高分子電解質膜補強基材に用いる多孔性シートを形成するアラミド樹脂にはメタ型アラミド樹脂及びパラ型アラミド樹脂からなるものがあるが、本発明には両者とも用いることができる。また、主成分がアラミド樹脂からなる共重合体でもブレンド体であっても構わない。

【0013】本発明において、アラミド樹脂からなる多孔性シートの形状は、アラミド繊維よりなる不織布、織物などの三次元網目状を有するもの、アラミド重合体である合成パルプが分散する構造の通気性のある紙様のシート、あるいはアラミド樹脂からなる細孔が多数開いたフィルムといった形状が好ましい。特にコーティングのし易さや高分子電解質ドープの含浸性、含浸量といった該補強基材により補強された電解質膜作製のし易さ及び該補強基材により補強された電解質膜のプロトン伝導性といった観点から、目付けが $5 \sim 40 \text{ g/m}^2$ の不織布が好適に用いられる。目付けが 5 g/m^2 未満であると補強基材としての強度を十分に保つことができない。また、目付けが 40 g/m^2 より大きいと膜厚が厚くなり、不織布の空隙率も低下する。このため膜抵抗が大きくなり高分子電解質膜の伝導度の低下を招く。

【0014】アラミド樹脂からなる多孔性シートをコーティングするフッ素樹脂としてポリテトラフルオロエチレン (PTFE) 及びこれを主成分にするフッ素樹脂が好適に用いられる。PTFEを主成分 (全体の50重量%以上、好ましくは80重量%以上) とするフッ素樹脂としては、例えばテトラフルオロエチレン-パーフルオロアルキルビニルエーテル共重合体 (PFA)、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体 (FEP)、が好適に用いられるが、これに限定されるものではない。

【0015】アラミド樹脂からなる多孔性シートにフッ素樹脂がコーティングされているかは光学顕微鏡、電子顕微鏡により観察できる。またラマン分光測定といった一般的な表面分析法でも確認できる。フッ素樹脂のコーティング量はコーティング前後の重量を測定することで見積もることができる。

【0016】本発明の高分子電解質膜補強基材は平均膜厚が $80 \mu\text{m}$ 以下で透気度が $10 \text{ sec}/100 \text{ cc} \cdot \text{in}^2$ 以下の透気度であることが好ましい。膜厚が $80 \mu\text{m}$ を超えると強度は上がるが、本発明の高分子電解質膜補強基材により補強された高分子電解質膜の膜厚が厚くなるため、電解質膜の水に対する膨潤度が低下することで膜抵抗が増加し好ましくない。透気度はガーレー法 (100 cc の空気が 1 in^2 の面積を 2.3 cmHg の圧力で透過するのに要する時間) により測定した値を示している。この値が $10 \text{ sec}/100 \text{ cc} \cdot \text{in}^2$ より大きいとポリマー溶液から塗工法による高分子電解

質の複合化が困難になるとともに、プロトン伝導性も十分に高めることが困難となる。

【0017】本発明の高分子電解質膜補強基材の製造法は特に制限はないが、①アラミド樹脂よりなる多孔性シートにフッ素樹脂の水分散液を含浸させ熱処理し、かかる多孔性シートをフッ素樹脂でコーティングする方法、②アラミド繊維にフッ素樹脂の水分散液を含浸させ熱処理し、かかる繊維表面をフッ素樹脂でコーティングし、得られた繊維を用いて不織布等の多孔性シートとしこれにかかる補強基材とする方法が挙げられる。ここでは製造の簡便さ等から前者が好ましい。以下、この方法について説明する。

【0018】このアラミド樹脂よりなる多孔性シートにフッ素樹脂の水分散液を含浸させ熱処理し、かかる多孔性シートをフッ素樹脂でコーティングする方法としては、例えば、アラミド不織布にフッ素系樹脂水分散液を含浸させ、ローラでしごくことで余分なフッ素樹脂水分散液を除去する。これを風乾させた後、フッ素樹脂の融点以上 380°C 以下で熱処理をおこなう。熱処理時に熱収縮がおこるので金型等で固定することが好ましい。熱処理は空気中でおこなっても構わないが、窒素雰囲気下等の酸素が存在しない環境でおこなう方が好ましい。酸素が存在すると熱処理中にアラミド樹脂からなる多孔性シートが酸化され変色、物性の低下を招くことがある。熱処理後水冷し急激に冷やす。これを風乾することで本発明における高分子電解質膜補強基材が作製できる。

【0019】コーティングに用いる該フッ素樹脂水分散液のフッ素樹脂固形分濃度は10～50重量%が好適である。フッ素樹脂固形分濃度が10重量%未満であるとアラミド樹脂からなる多孔性シートを構成している樹脂 (不織布の場合、それを構成する繊維) の表面をフッ素樹脂で十分覆うことができず、耐酸化性が十分に改善されない。また、フッ素樹脂固形分濃度が50重量%より大きいとフッ素樹脂がアラミド樹脂からなる多孔性シートの孔を塞いでしまい、プロトン伝導性高分子電解質と複合化が困難になり好ましくない。また、複合化できても膜抵抗が増加し電気特性が好ましくない。

【0020】アラミド樹脂からなる多孔性シートにフッ素樹脂水分散液を含浸させた後に熱処理をおこなうが、熱処理はフッ素樹脂の融点以上 380°C 以下で行うのが好ましい。フッ素樹脂の融点未満であるとフッ素樹脂が溶解せず、フッ素樹脂で多孔性シートの表面を十分に覆うことは難しい。ここで、多孔性シートの表面とは、多孔性シートの両表面以外に、シート内部の孔の表面や、不織布の場合各繊維の表面を含む。また、 380°C より高い温度で熱処理をおこなうと、熱処理中にかかる多孔性シートの熱分解がおこり物性の低下を招く。熱処理時間は3～10分が好ましい。3分未満であると樹脂表面に付着したフッ素樹脂が熔融し流動することで表面をコーティングするのに十分な時間がない。また、10分よ

り長いと熱処理によりかかる多孔性シートの劣化がおこり物性面で問題が生じる。

【0021】このようにして得られた多孔性シートは、耐酸化性が十分に改善される程度にフッ素樹脂により実質的に覆われ、透気度は $10 \text{ sec} / 100 \text{ cc} \cdot \text{in}^2$ 以下であるものが電気特性の観点から好ましい。

【0022】該高分子電解質膜補強基材により補強されたプロトン伝導性高分子電解質膜について述べる。

【0023】該プロトン伝導性高分子電解質膜は、上記高分子膜補強基材とプロトン伝導性ポリマーとが組み合わされてなる複合体であり、 300°C 以上の力学的な耐熱性を有している点が特徴である。力学的な耐熱温度は機械的熱的特性分析 (TMA) で測定できる。ここでは、該プロトン伝導性高分子電解質膜 (膜厚約 4.5 mm 、幅 5 mm 、長さ 25 mm の短冊状) に 1 g の荷重で $10^\circ\text{C}/\text{分}$ の速度で温度を昇温させ、膜が破断するかあるいは膜が 10% 伸びる温度を力学的な耐熱温度とした。この温度が 300°C 未満では、異常反応等により電池内部の温度が急激に上がった際の電池の安全性を保証できなくなり好ましくない。

【0024】該プロトン伝導性高分子電解質膜は、例えば上記高分子電解質膜補強基材にプロトン伝導性ポリマーを含浸させ、乾燥することによって製造することができる。プロトン伝導性ポリマーとしては「ナフィオン」に代表されるパーフルオロスルホン酸樹脂、ポリスチレンスルホン酸、スルホン酸基が導入されたポリスルホン、ポリエーテルスルホン、ポリスルホン等が挙げられるが、これらに限定されるものではない。

【0025】

【実施例】以下、本発明の内容を実施例を用いて詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

<耐酸化性モデル評価>実施例における耐酸化性の評価法を述べる。ただし、耐酸化性の評価はこれに限定されるものではない。本発明は耐酸化性の向上のためアラミド不織布をフッ素樹脂でコーティングしているが、不織布の耐酸化性の評価は "Proceedings of the Symposium on Electrode Materials and Process for Energy Conversion and Storage", Vol. 77 (6), p. 314 (1977), The Electrochemical Society に記載されている方法を参考にした。 30% 重量%の過酸化水素水に 20 ppm の硫酸鉄 (II) (FeSO_4) を混ぜたいわゆる Fenton 試薬中に不織布を浸漬し 68°C で熱処理する。このように処理した不織布の引張最大応力の経時変化により不織布の耐酸化性を評価することができる。引張最大応力は引っ張り試験での最大応力である。24時間熱処理後の不織布の引張最大応力を未処理の不織布の引張最大応力

で割った値 (百分率で示す) を引張最大応力維持率とし、これを耐酸化性の指標とした。

【0026】【実施例1】メタ型アラミド繊維 (商品名: コーネックス、帝人株式会社製) からなる平均膜厚が $40 \mu\text{m}$ 、目付けが $20 \text{ g}/\text{m}^2$ の不織布を乾式抄造法により作製し、これに固形分濃度が 30% のポリテトラフルオロエチレン (PTFE、融点 327°C) 水分散液 (ダイキン工業製) を含浸させ、ローラでしごき、風乾させた。この不織布を金型に固定し、 340°C で10分間熱処理をおこない高分子電解質膜補強基材を作製した。この高分子電解質膜補強基材の平均膜厚は $50 \mu\text{m}$ 、透気度は $0.1 \text{ sec} / 100 \text{ cc} \cdot \text{in}^2$ であった。この不織布について上で述べたような方法で耐酸化性の評価をおこなった。引張最大応力維持率は 84.6% であった。結果を図1に示す。

【0027】【実施例2】メタ型アラミド繊維 (商品名: コーネックス、帝人株式会社製) からなる平均膜厚が $40 \mu\text{m}$ 、目付けが $20 \text{ g}/\text{m}^2$ の不織布を乾式抄造法により作製し、これに固形分濃度が 30% のテトラフルオロエチレン-ヘキサフルオロプロピレン共重合体 (FEP、融点 270°C) 水分散液 (ダイキン工業製) を含浸させ、ローラでしごき、風乾させた。この不織布を金型に固定し、 300°C で10分間熱処理をおこない高分子電解質膜補強基材を作製した。この高分子電解質膜補強基材の平均膜厚は $50 \mu\text{m}$ であった。透気度は $0.1 \text{ sec} / 100 \text{ cc} \cdot \text{in}^2$ 。この不織布について上で述べたような方法で耐酸化性の評価をおこなった。引張最大応力維持率は 81.3% であった。結果を図1に示す。

【0028】【比較例1】メタ型アラミド繊維 (商品名: コーネックス、帝人株式会社製) からなる平均膜厚が $40 \mu\text{m}$ 、目付けが $20 \text{ g}/\text{m}^2$ の不織布を乾式抄造法により作製し、上で述べたような方法で耐酸化性の評価をおこなった。この不織布の透気度は $0.04 \text{ sec} / 100 \text{ cc} \cdot \text{in}^2$ 、引張最大応力維持率は 27.3% であった。結果を図1に示す。実施例1、2及び比較例1から本発明の高分子電解質膜補強基材であるフッ素樹脂をコーティングしたアラミド不織布は明らかにアラミド不織布に比べ耐酸化性が改善された。

【0029】【実施例3】実施例1で作製し高分子電解質膜補強基材をポリエチレンテレフタレートフィルム上に置き、その上から $10 \text{ wt.}\%$ のナフィオン溶液 (Aldrich社) を $200 \mu\text{m}$ のクリアランスのドクターナイフでキャストした。ついでこれを風乾することにより該補強基材で補強されたプロトン伝導性高分子電解質膜を作製した。このプロトン伝導性高分子電解質膜の力学的な耐熱温度は 400°C 以上であった。このプロトン伝導性電解質膜について上で述べたような方法で耐酸化性の評価をおこなった結果、引張最大応力維持率は 82.1% であった。

【0030】〔実施例4〕実施例2で作製し高分子電解質膜補強基材をポリエチレンテレフタレートフィルム上に置き、その上から10wt. %のナフィオン溶液（Aldrich社）を200 μ mのクリアランスのドクターナイフでキャストした。風乾することで該補強基材で補強されたプロトン伝導性高分子電解質膜を作製した。このプロトン伝導性高分子電解質膜の力学的な耐熱温度は400℃以上であった。このプロトン伝導性電解質膜について上で述べたような方法で耐酸化性の評価をおこなった結果、引張最大応力維持率は79.4%であった。実施例3、4から本発明の高分子電解質膜補強基材をパーフルオロスルホン酸樹脂と複合化させたプロトン伝導性電解質膜も本発明の高分子電解質膜補強基材と同等の耐酸化性を維持することが示された。そしてフッ素樹脂をコーティングしたアラミド不織布は、アラミド不織布に比べ、耐酸性、耐加水分解性も改善された。

【0031】〔実施例5〕ガス拡散電極として0.38mg/cm²の白金を担持させた米国E-TEK INC製の電極を用い、これを直径30mmに打ち抜いて用いた。実施例3で得られた高分子電解質膜を、沸騰したイ

オン交換水中に2時間浸漬し、かかる膜を含水状態とした後、表面の過剰な水を拭き取り、かかるガス拡散電極2枚で挟み込み、100℃にて9.8MPa（100kgf/cm²）で3分間加圧し電極接合体を得た。得られた電極接合体について、加湿水素及び酸素を供給し80℃加熱下で燃料電池出力特性を評価した。10ケの単セルを作製したが、短絡やガスリークなどの欠陥は一つもなく、0.7A/cm²で0.65Vの性能が得られた。

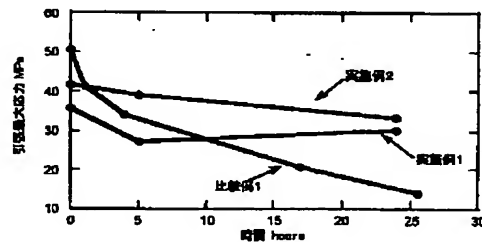
10 【0032】

【発明の効果】以上詳述してきたように本発明によれば、フッ素樹脂でコーティングすることでアラミド樹脂からなる多孔性シートの耐酸化性、耐酸性、耐加水分解性を向上させ、アラミド樹脂からなる多孔性シートを、特に固体高分子型燃料電池用に好適な高分子電解質膜補強基材として用いることが可能となった。

【図面の簡単な説明】

【図1】図1は実施例1、2及び比較例1、2の不織布の耐酸化性評価における引張最大応力の経時変化を示したものである。

【図1】



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